ABSTRACT

Studies of Reactions of Some μ-Superoxo Complexes of Cobalt(III) in Aqueous Sulfite Solution - a study of some complex electron transfer processes in solution

The stoichiometry and kinetics of the reaction of a series of binuclear cobalt(III) amine dioxygen complexes in aqueous acidic sulfite solution have been extensively studied. The μ-superoxo complexes are reduced in solution by two bisulfite ions to produce the corresponding μ-sulfato complexes and a bisulfite radical.

In the case of the dibridged complexes,
$[(H_3N)_4Co.\mu\text{-}(NH_2,O_2).Co(NH_3)_4]^{4+}$
$[(en)_2Co.\mu\text{-}(NH_2,O_2).Co(en)_2]^{4+}$ and
$[(tren)Co.\mu\text{-}(NH_2,O_2).Co(tren)]^{4+}$
the reductive addition reaction yields stable μ-sulfato complexes which have been isolated and characterised as the μ-amido-μ-sulfato complex. Cobalt(II), mononuclear cobalt(III) and free sulfate (in excess) are also formed. While the amount of μ-sulfato complex formed is constant (75 (± 3) %), the amount of cobalt(II) formed varies according to the stability of the corresponding μ-peroxo complex in acidic solution. Over the wide range of conditions studied, the presence

or absence of air, the pH of the solution and the total sulfite concentration have no effect on the stoichiometry of the reaction products. The formation of cobalt(II) and mononuclear cobalt(III) results from the intervention of the incipient bisulfite radical, resulting in the initiation of a whole series of fast follow-up electron transfer reactions.

The single-bridged complexes, $[(H_3N)_5CoOOCo(NH_3)_5]^{5+}$ and $[(H_3N)trenCoOOCotren(NH_3)]^{5+}$, on the other hand, do not have a second bridge to stabilize the μ-sulfato complex, which, as soon as it is formed, is rapidly reduced by the incipient bisulfite radical to produce a sulfato(amine)cobalt(III) complex and cobalt(II) in equimolar quantities. This sulfato product is stable in the case of the bis(pentaammine) compound, but is slowly reduced to cobalt(II) in the case of the (ammine)tren complex.

The mechanism of the μ-superoxo/sulfite reaction involves the attack of two bisulfite ions on the superoxo complex. Rate constants, $k(= M^{-2}\ s^{-1})$ for the third-order process at 25°C vary in the order bis(pentaammine) (367 ±4) < bis(tetraammine) (513 ± 5) < bis(bis-ethylenediamine) (2240 ± 40) < bis(tris-2-aminoethylamine) (2930 ± 30) < bis((amine)tren) (20100

± 200). The observed rate trends suggest that both steric and electronic effects might be important in determining the magnitude of the rate constants. The variation in rates appears to be mainly entropic in origin and suggest that electrostriction effects on solvent molecules by the highly charged metal complexes, which releases them on activation with the negatively charged sulfite species, are important in determining the activation parameters. Transition states for the reaction of both the single-bridged and the dibridged complexes with bisulfite ions have been proposed.

The observation of the same rate law in the reduction of the single and dibridged μ-superoxo complexes, which possess an electronically similar redox reactive site, in addition to the obedience of the activation parameters to an isokinetic plot of $\Delta H^{\#}$ against $\Delta S^{\#}$ suggest that a common mechanism of μ-superoxo reduction by aqueous sulfite is operative. An isokinetic temperature of 342 (± 23) K and a free energy of activation of 12.4 (± 0.8) kcal/mole are obtained from the slope and intercept of the isokinetic plot, respectively.